Carbon nanotube synthesis from germanium nanoparticles on patterned substrates

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***Abstract*— Controlled synthesis of carbon nanotubes (CNTs) is highly desirable for nanoelectronics applications. To date, metallic catalyst particles have been deemed unavoidable for the nucleation and growth of any kind of CNTs. Ordered arrays of nanotubes have been obtained by controlled deposition of the metallic catalyst particles. However, the presence of metal species mixed with the CNTs represents a shortcoming for most electronic applications, as metal particles are incompatible with silicon semiconductor technology. In the present paper we report on a metal-catalyst-free synthesis of CNTs, obtained through Ge nano-particles on a Si(001) surface patterned by nanoindentation. By using acetylene as the carbon feed gas in a low-pressure Chemical Vapor Deposition (CVD) system, multi-walled carbon nanotubes (MWNT) have been observed to arise from the smallest Ge islands. The CNTs and the Ge three-dimensional structures have been analysed by SEM, EDX and AFM in order to assess their elemental features and properties. EDX and SEM results allow confirmation of the absence of any metallic contamination on the surface, indicating that the origin of the CNT growth is the Ge nanocrystals.**

I. INTRODUCTION

Carbon nanotubes (CNT) are expected to play an important role in future generation electronics. This considerable interest is due to their unique electrical and mechanical properties. An individual carbon nanotube outclasses any other material for in relation to electrical, optical, thermal and mechanical properties, showing indeed super-high current-carrying capacity, ballistic electron transport and good field-emission properties. Several CNT-based devices have already been demonstrated like field-effect transistors, nonvolatile random-access memories, sensors, field-emission displays, organic solar cells [1]. For CNT production, Chemical Vapor Deposition (CVD) has been proven as the most reliable and effective method, also because of its ease and economy. Importantly for electronics, CVD allows controlled growth of CNTs on different substrates [2]. In a typical CVD process, CNTs are produced by a catalytic decomposition of one or more volatile precursors, which decompose and react with a layer of catalytic particles pre-deposited on a surface. Large arrays of CNTs have been grown by CVD on different substrates, in various shapes and with a certain degree of control [1]. When hydrocarbons are used as precursors, metal elements are indispensable as catalyst for the growth of CNTs. The most used are iron-group elements (Fe, Co, Ni) and their alloys. Such metal particles can be deposited and assembled on various substrates with a high degree of control, leading to highly-ordered growth of CNTs as carpets and geometric architectures [1]. The high rate of CNT growth from metal catalysts is due to ease of forming nano-sized particles that can act as templates for cap formation and enhance the synthesis of single and multi-walled carbon nanotubes. Recently, however, Yazyev et al. have investigated the role of the chemical composition of the catalytic nanoparticles in the CVD growth of CNTs, considering late-transition (Ni, Pd, Pt) and coinage (Cu, Ag, Au) metals [3]. As a matter of fact, a wider range of materials than expected seems to favor CVD growth of CNTs, even if with different requirements and results.

For applications such as sensors or memories the presence of metal species is detrimental to their performance. Most transition metals such as Ni or Fe create deep-level defects in the bandgap of Si and result in unwanted trap states. Unfortunately, it is also very difficult to remove the metal catalyst contamination in post-processing, without reducing the quality and thus the performances of a device. However, after the first attempt by Uchino and coworkers [4] to grow CNTs by hydrocarbon decomposition through SiGe nanostructures, recent studies claim that only a nano-scale curvature is necessary for growth. [5]. This opens up routes for a wide range of materials to act as catalysts. In particular, it has been demonstrated that it is possible to obtain CNT formation on semiconductor substrates as SiC, Ge, and Si from semiconductor nano-particles of the same materials [5, 6]. This method still suffers from low yields and needs to be further improved, given the relevance of the implications. Another group has proposed a simple and effective method for growing SWNTs via a metal-catalyst-free CVD process on a sputter deposited SiO_2 film, by which it is possible obtaining metal-free, pure, and dense SWNTs [7].

In order to increase the density of the CNTs grown from semiconductor particles, a viable route might be a pre-patterning stage of the substrate. Precise and high-resolution techniques such as electron-beam lithography and focused ion-beam FIB patterning can be effectively used for leading the assembly of these nanoparticles. However, these are relatively expensive and time-consuming. In this study, we report

substrate pre-patterning using nanoindentation with subsequent CVD growth of CNTs from Ge nanoparticles positioned on the pre-patterned Si surface. Nanoindentation allows precise patterning without complicated lithography. Additonally, location specific growth of CNTs adsent of metallic impurities is feasible.

II. Experiment

A Si(001) sample was patterned by nanoindentation in a specific areausing a diamond tip (Berkovich) fitted to a Hysitron Triboindenter. A grid of 16 indents per side was created on the surface; all the impressions are triangular-shaped and exactly reproduce the profile of the tip. In Fig. 1 an AFM image of the nanoindented area is shown. The triangular pits have a typical side about 600 nm long, a depth of a least 30 nm, and a relative distance of about 1 μm. The patterned region is then about 15x15 μm^2. After a cleaning stage by cyclical ultrasonic baths in ethylic alcohol and high-pure deionised water (ρ=18 MΩ cm), the sample was annealed in ultra-high vacuum (p=4 10-11 Torr) at 600 °C for 30 minutes. A few flashes at 1100 °C followed, aiming at reconstructing the surface by re-epitaxy of Si. Once a good clean and reconstructed surface was obtained, Ge has been evaporated, keeping the sample at 580 °C up to a total coverage of 13 monolayers. The substrate was then extracted from the UHV vessel and mounted in the nanotube growth chamber. CNTs synthesis was performed by employing acetylene (C_2H_2) at low-pressure (12 Torr) while keeping the substrate at 750 °C. The growth process lasted for 20 minutes and a flux of Ar was then kept for 5 minutes before taking out the sample.

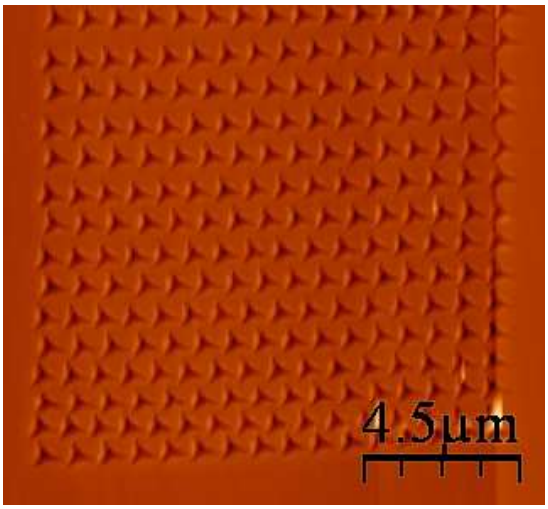

Figure 1. Atomic force microscope image of a nanoindented area 15x15 μm^2 on Si(001).

III. Results and Discussion

After the Ge evaporation, Ge islands appeared all over the surface, both on pristine and patterned areas (Fig. 2). As expected [8, 9] in the patterned areas the islands density is higher (about 1.2 10^{12} dots/cm^2 near the indent versus 1.4 10^{11} dots/cm^2 far from the pits) while the islands size is around a mean value of 200 nm constant on the whole area. The higher value of islands density near the pits can be explained by using a model which relates the nucleation probability to the elastic energy involved in the creation of a Ge nanoisland on a Si substrate with a lower lattice constant. It is possible to show [8, 9] that Ge nanocrystals nucleate preferentially on the edge of the indents where the strain release is higher as shown in Fig 2c and 2d.

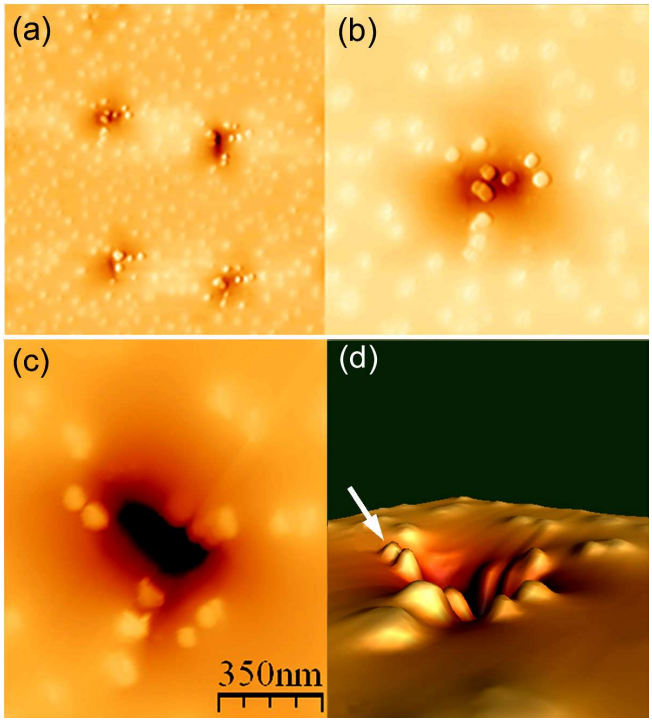

Figure 2. Atomic force microscope images of the indented Si(001) substrate after the deposition of 13 ML of Ge at T=580 °C. (a) 5x5 μm^2 (b) 2x2 μm^2 (c) (1x1 μm^2) (2D) (d) 3D representation of image (c). Ge island indicated by an arrow: width 70 nm, height 30 nm.

The annealing at 750°C during the CVD stage favours Ge diffusion, producing the formation of an ordered distribution of domes over the indents (Fig. 3).

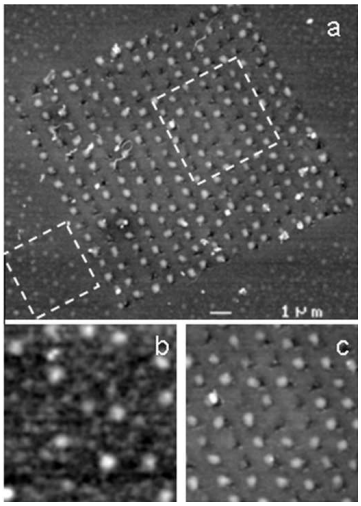

Figure 3. SEM images of the indented Si(001) substrate after the growth of CNT to show the Ge islands modifications (a) 15x15 μm^2 showing patterned and non patterned areas. (b) enlargement of a non patterned area (3x3 μm^2). (c) enlargement of a (5x5 μm^2) patterned area. Notice the ordering and the uniform island size in (c).

In fig.3 is evident the islands ordering in the patterned region (panel c) while in non-patterned areas the nucleation sites of islands are random. The islands in the pits appear much larger than the islands outside, indicating a ripening process which is certainly favored by the indentations. This result illustrates that the underlying patterning leads not only the nucleation but also the ripening process and the islands positioning seems to point to a specific optimum in terms of relative distance between holes. In fact other areas with arrays of indents of different pitches (0.75, 1.5, 2 µm) do not show such an ordered assembling of Ge islands as confirmed by other experiments [10]. The optimum separation of indents is dependent of the diffusion length of Ge along the Si surface suring annealing. In spite of the island ripening during the Chemical Vapor Deposition some growth of MWNTs is observed originating from the small (<50nm) residual nanoparticles between the indents. It is interesting to notice that the carbon nanotubes nucleate only from Ge nano-particles in the patterned area (figure 4a), while no tubes are visible in the non-patterned area (where the Ge particles are larger). The samples have been analysed by SEM, EDX and AFM. The EDX spectrum obtained from our sample is reported in figure 4b. It clearly indicates that metal species are not present in the patterned area, as only the Si signal has been detected.

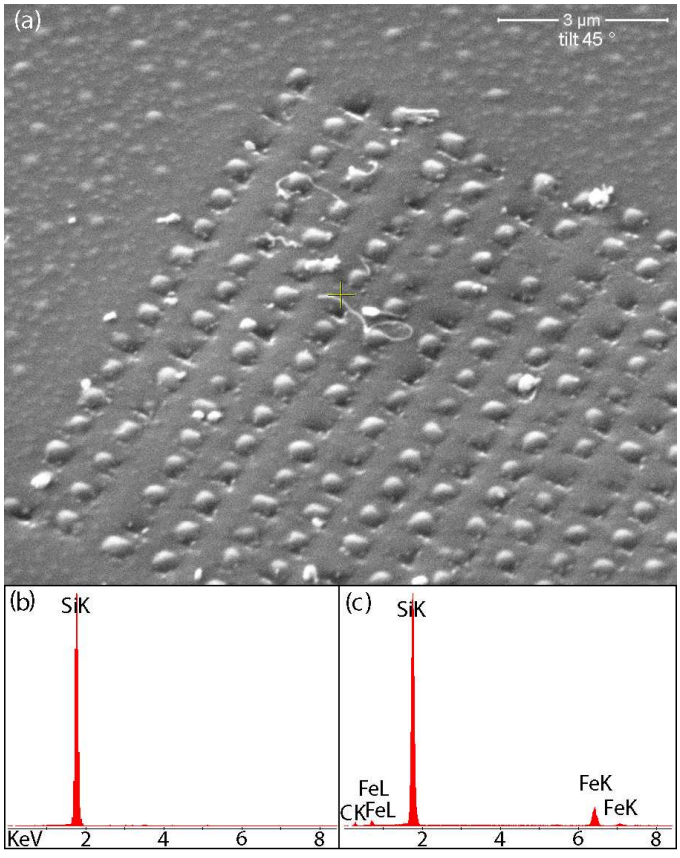

Figure 4. a) Scanning electron microscope image of the nanoindented area after the Ge depostion and CNTs growth. A few tubes nucleated from Ge nanoparticles sitting on the edge of the indents. b) EDX of the same area, showing only a Si peak. c) EDX of a conventional sample with a few CNTs grown with Fe catalyst particles.

As a comparison in figure 4c we report a spectrum obtained from a similar sample where Fe catalysts have been used for the growth. In this case the Fe signal (K and L line) is clearly detected. This points out that the presence of Ge nanodots on the sample surface is sufficient for the growth of carbon nanotubes, confirming that Ge can act as catalyzer of the reaction, as reported by Takagi's group [5].

In a typical metal-catalyzed CVD, unless the catalyst nanoparticles have been deposited under controlled way, carbon nanotubes grow entangled and in high density; conversely, in our experiment only a few nanotubes appear, but they sprout only in specific positions. Figure 5 reports a HR-SEM image on small area from figure 4, which shows Ge nanoparticles and CNTs. It can be observed that CNTs only grow from Ge nanoparticles less than 50 nm in diameter, indicating that the dimension of Ge nanoparticles influences the CNTs yield. This result is very interesting, as it leads to conclude that also Ge nanoparticles larger than the ones used by Takagi and coworkers are able to catalyze the carbon nanotube growth. A detailed study of the optimum size of nanoparticles and of their crystal structure is in progress [10]. Pre-pattering down to 20 nm feature sizes will confirm that growth occurs from nanoparticles around this size.

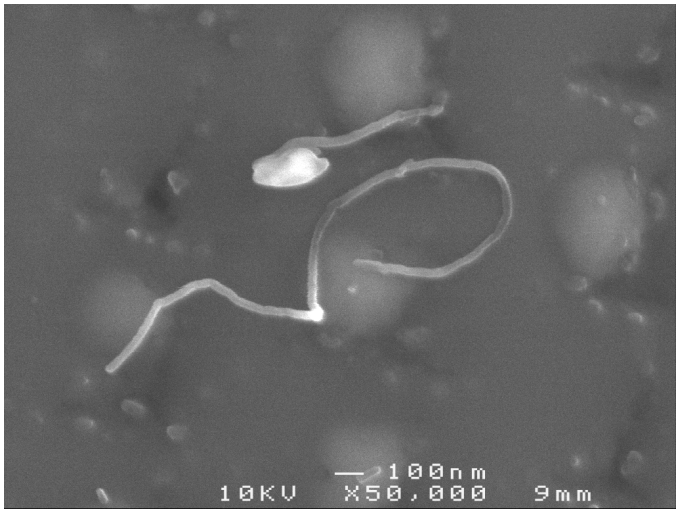

Figure 5. Hi-resolution scanning electron microscope image of a MWNT nucleated from a Ge nanoparticle.

IV. Summary and Conclusion

In the present paper, we report on a metal-catalyst-free synthesis of CNTs on a Si(001) surface patterned by nanoindentation. The results illustrate how it is possible to control the growth of CNTs without the use of a metal catalyst, by leading the assembly of Ge nanoparticles. By pre-pattering the wafer with indents down to ~50 nm dimensions, we expect that order arrays of CNTs can be formed from an array of Ge nanparticles. Our method still suffers from low yield, but can be further improved by using a more dense pattern obtained by Focused Ion Beam [11], for example.

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